

S&C FY02 ANNUAL REVIEW MEETING

In-Situ Real Time Measurements of Melt Constituents

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DOE's Office of Industrial Technologies

- **Sensors and Controls**

SENSORS & CONTROLS



- **Inventions and Innovations**

INVENTIONS & INNOVATION



- **Aluminum**

Aluminum
Industry of the Future



- **Glass**

Glass
Industry of the Future



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New York State Support

 NYSERDA

NYSERDA



 NYS DED



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Industrial Participants

- **Commonwealth Aluminum**
- **Century Aluminum**
- **Arco Aluminum**
- **Crucible Specialty Metals (steel)**
- **PPG Industries (fiberglass)**
- **Fenton Art Glass (specialty glass)**
- **Hugo Neu (metal recycler)**
- **Crestwood Metals (metal recycler)**
- **Stein Atkinson Stordy (overseas marketing)**

Companies Expressing Interest

- **Alcoa**
- **Hydro Aluminum**
- **Tennessee Aluminum Processors**

Program Accomplishments

- LIBS Probe developed for *in-situ* analyses of molten aluminum and other materials
- Melt composition can be measured at any point below or on top of the melt surface
- Laboratory and pilot scale probes built
- First LIBS data ever recorded from within molten aluminum
- Demonstrated laboratory scale LIBS Probe at Alcoa plant during DOE Showcase, August 2001
- Will Demonstrate LIBS Probe at Commonwealth Aluminum during upcoming DOE Showcase

Program Accomplishments

- **For Aluminum, Commercialization Plan Completed**
- **MOU for Licensing Agreement Signed for Overseas and US Market**
- **Patent Application Filed**

Program Accomplishments

- **Other Opportunities**

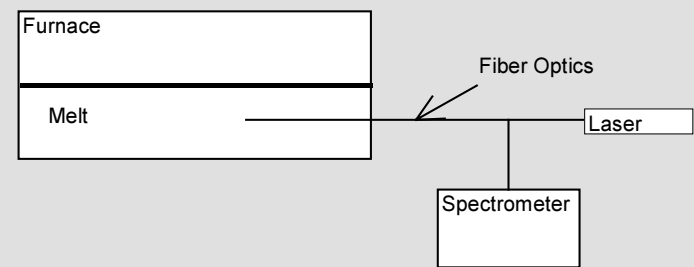
- Glass Batch, Cullet – DOE Funding
- Molten Steel – NYSERDA Funding
- Alloy Identification – NY DED Funding

Recent Accomplishments

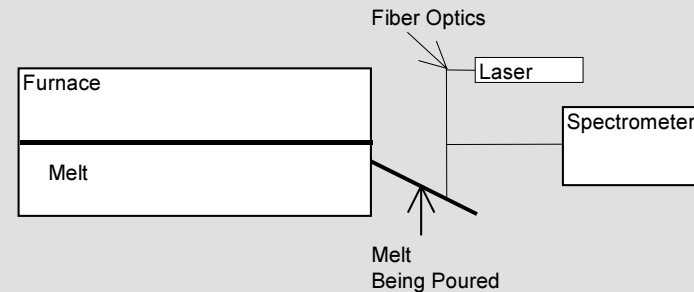
- **Equipment upgrades**
 - Industrial grade fiber optic coupled laser
 - Upgraded Spectrometer System
 - Upgraded Cooling System
- **Novel optical layout**
 - Increased accessible wavelength range
 - Increased laser throughput
- **Optical upgrades boost signal 5-10x**

Project Description

- Develop an in-situ and real time sensor for measuring the elemental constituents of metal and glass melts
- Sensor Capabilities
 - **Can be inserted directly into the melt to any depth and at different insertion angles**
 - **Collects real-time continuous concentration data**
 - **Installed sensor cost acceptable to industry**



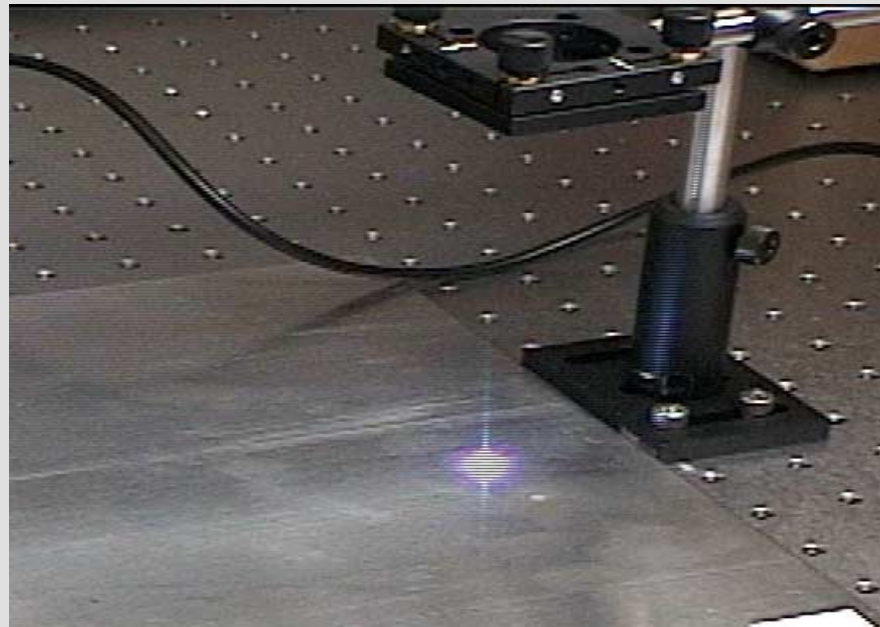
A. Measurements Made Within Furnace



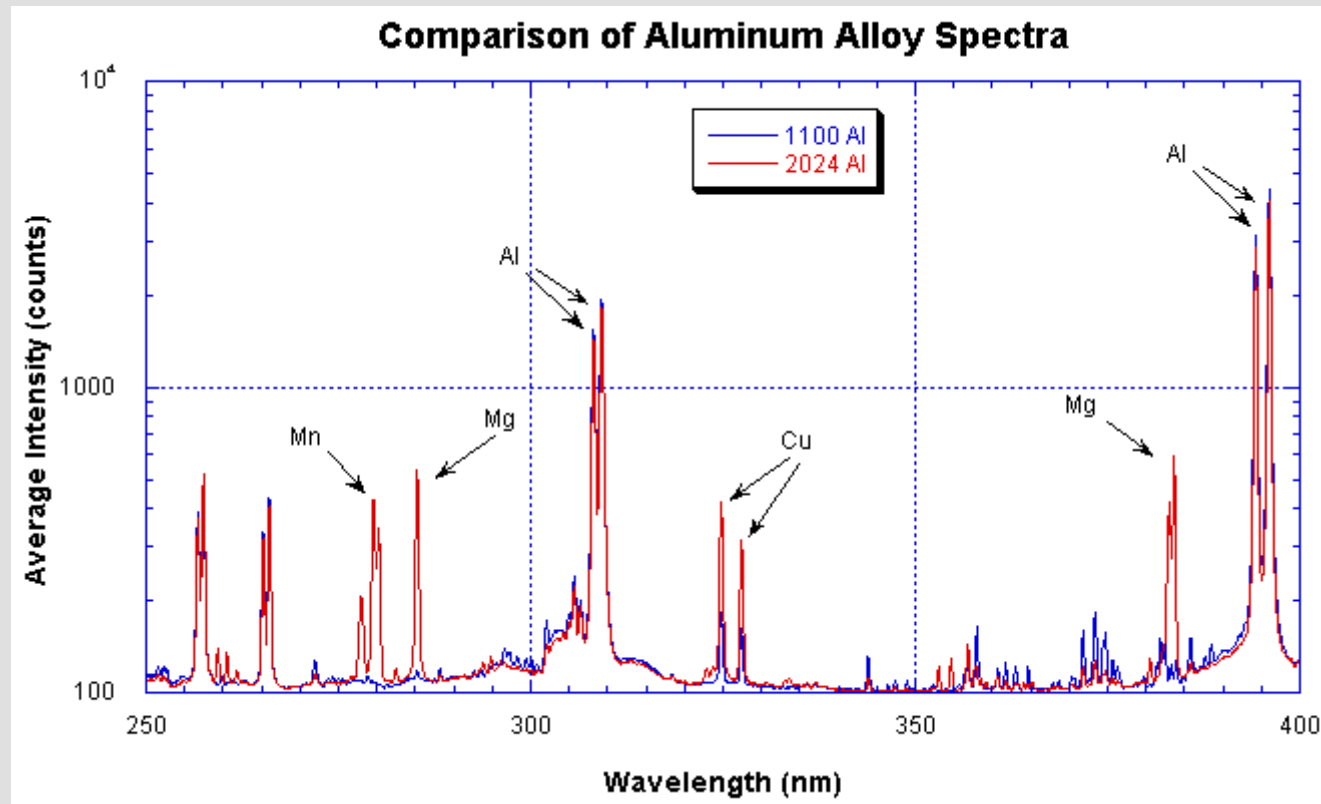
B. Measurements Made During Pour

Project Description

- **LIBS=Laser Induced Breakdown Spectroscopy**
- **Tightly focused laser is used to vaporize a minute amount of material resulting in a plasma**
- **UV light emitted by the plasma is analyzed using a spectrometer**
- **The strength of emissions from individual elements in the spectrum are directly related to their concentration in the material**



Project Description



Spectrometer gathers the ultraviolet light and spreads it, like a prism, into a spectrum where the contribution of each element can be seen

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Project Description

■ LIBS Advantages

- Fast
 - 10-50 Measurements/second with commercial low cost (~\$10k) solid state lasers
- Accurate
 - Able to measure concentrations at fractions of a percent
- Applicable to a wide range of materials
 - Metals
 - Glass
- Proven
 - Extensive literature on use of the process in lab environments

Project Objectives/Goal

- **Problem Statement – Off line sampling of melt constituents leads to:**
 - Excessive melting times
 - Quality problems
 - Increased energy use and emissions
 - Wasted product

- **Objectives**
 - Year 1: Develop laboratory scale LIBS probe for molten aluminum
 - Year 2: Develop pilot LIBS probe for molten aluminum
 - Year 3: Develop commercial probe for installation at aluminum plants

Project Objectives/Goal

- **Overall goal**

- Development of an *in-situ* and real time immersible LIBS probe capable of measuring elemental constituents in molten aluminum.
- Sensor has sufficient sensitivity and accuracy to remove the need for time consuming laboratory analyses, chemical treatments, or other processes that hinder productivity

Technical Risks/Innovation

- **Technical risks**

- Development of *in-situ* optical probe for hot opaque melts
- Automating LIBS analysis
- Bringing LIBS equipment to plant floor
- Packaging LIBS so that it operates as reliably as other sensor equipment and requires little additional employee training

Technical Risks/Innovation

■ Innovation

- Ceramic probe enables LIBS measurements below melt surface
- Fiber optic coupling removes sensitive equipment from plant floor
- Novel optical design for constraining sensor dimensions
- Automated LIBS analysis software that does not require calibration
- Industrial quality components

Technical Risks/Innovation

- **Advancement of state-of-the-art; over competition**
 - In-situ analysis of molten material is not otherwise available
 - LIBS probe can collect data to enable:
 - In-line alloying
 - Operating furnaces in a continuous rather than batch mode
 - Advanced furnace and process modeling

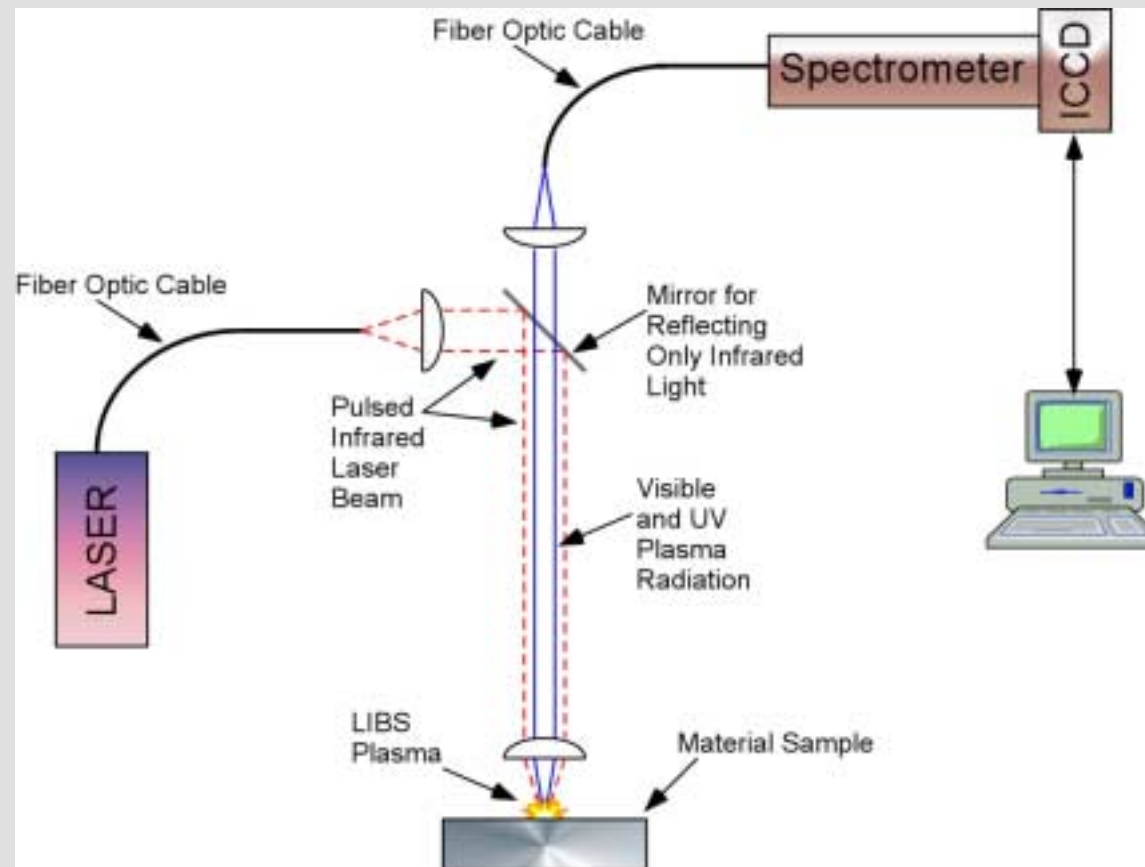
Task Performance

Past Technical Milestones

Milestone	Due Date	Completion Date	Comments
1-1 Fiber Optic Design and Construction	9/99	12/99	
1-2 Testing	3/00	12/00	
1-3 Cost Evaluation	3/00	3/00	
2-1 Pilot Scale Probe Construction	10/00	5/01	
2-2 Furnace Modifications	10/00	5/01	
2-3 Testing	2/01	5/01	

Progress Toward Performance Goals

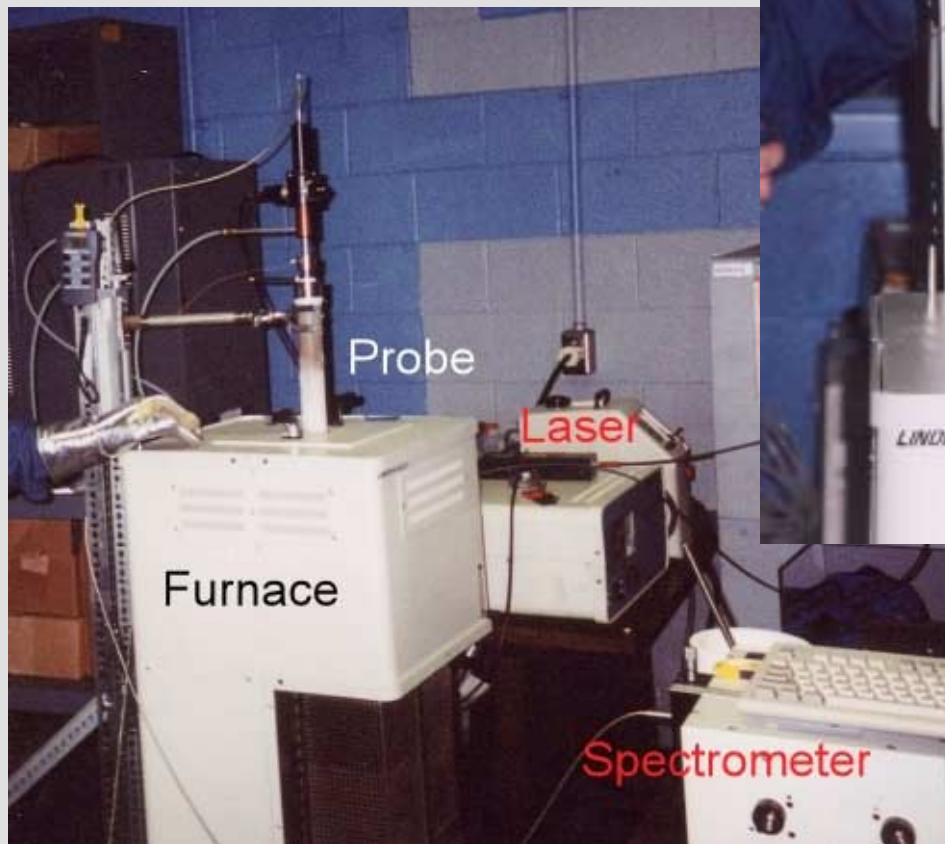
- Optical Design



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DOE Showcase Probe

Spanish Forks, UT

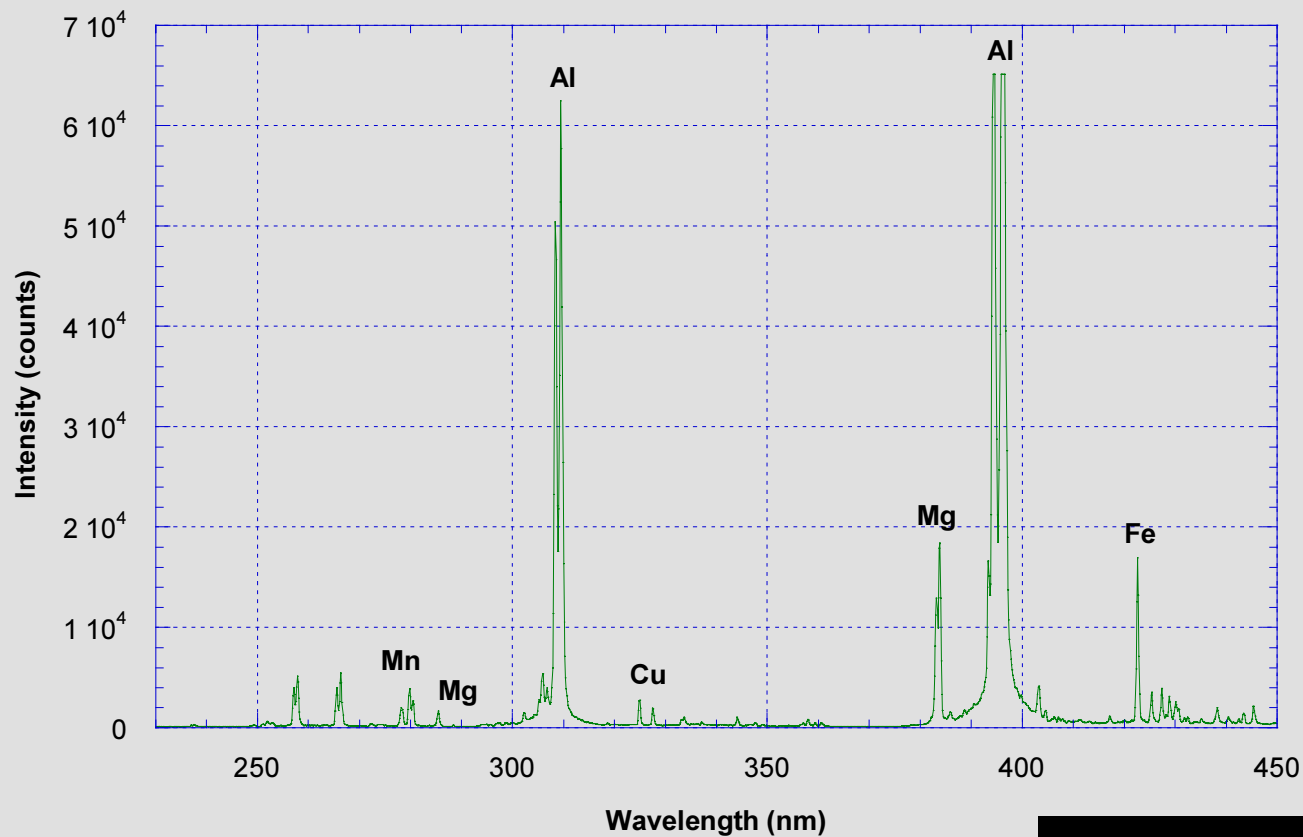


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Molten Aluminum LIBS Spectra

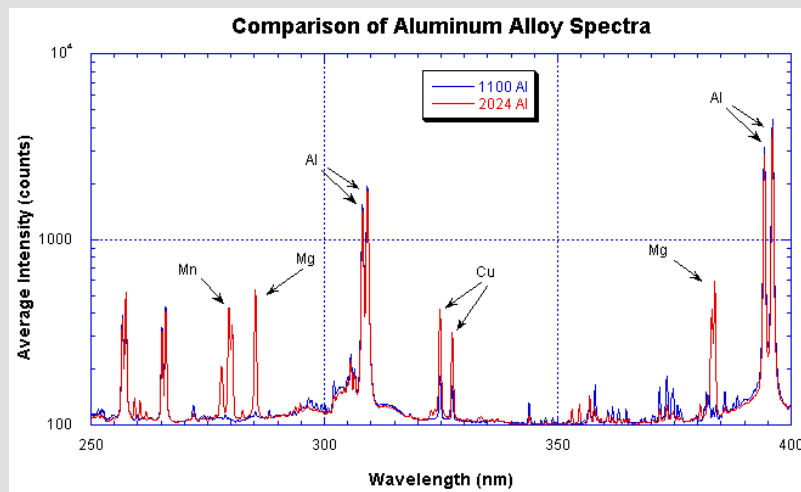
- LIBS spectra collected from beneath surface of aluminum melt



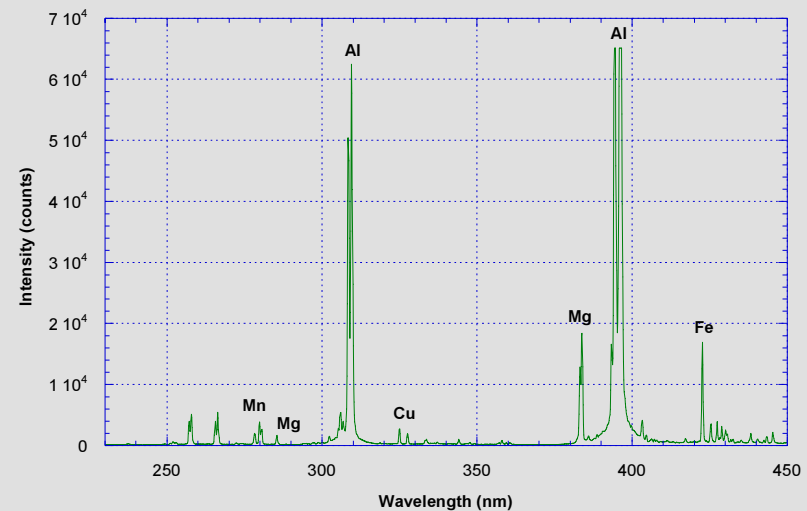
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Major Accomplishment

■ Deployment of LIBS Below Surface of Molten Metal



Solid Material: Proven Technology



Molten Material: New Technology

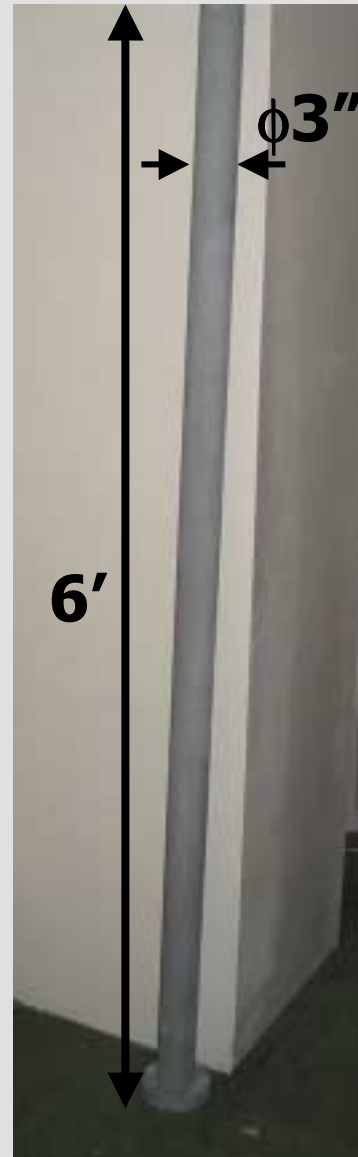
- First ever LIBS Data below surface of molten aluminum
- Patent Pending Design

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Pilot Scale Probe

■ Pilot Scale Probe Tests

- Unique design required working with ceramics fabricator
- 6' length suitable for pilot and full scale test
- 3" OD suitable for off-the-shelf insertion and retraction mechanisms

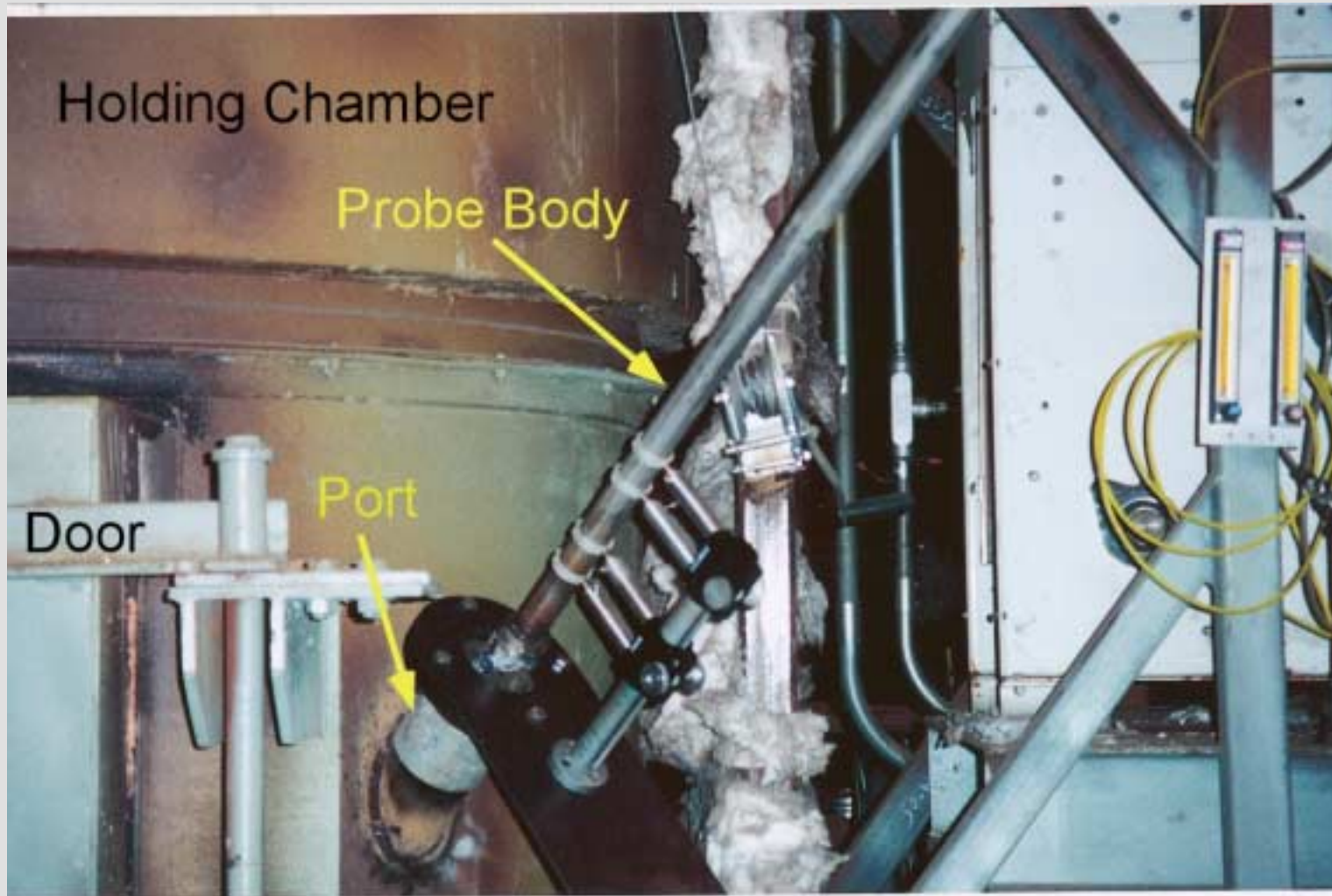


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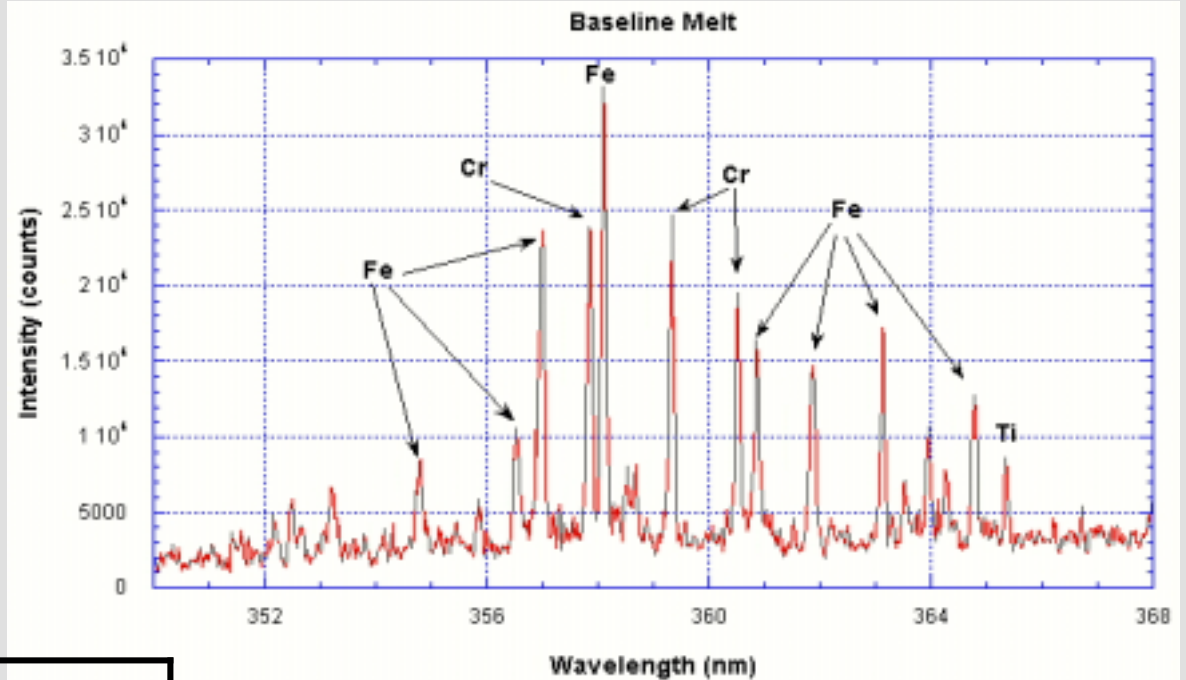
VFM



Installation at Pilot Scale Facility



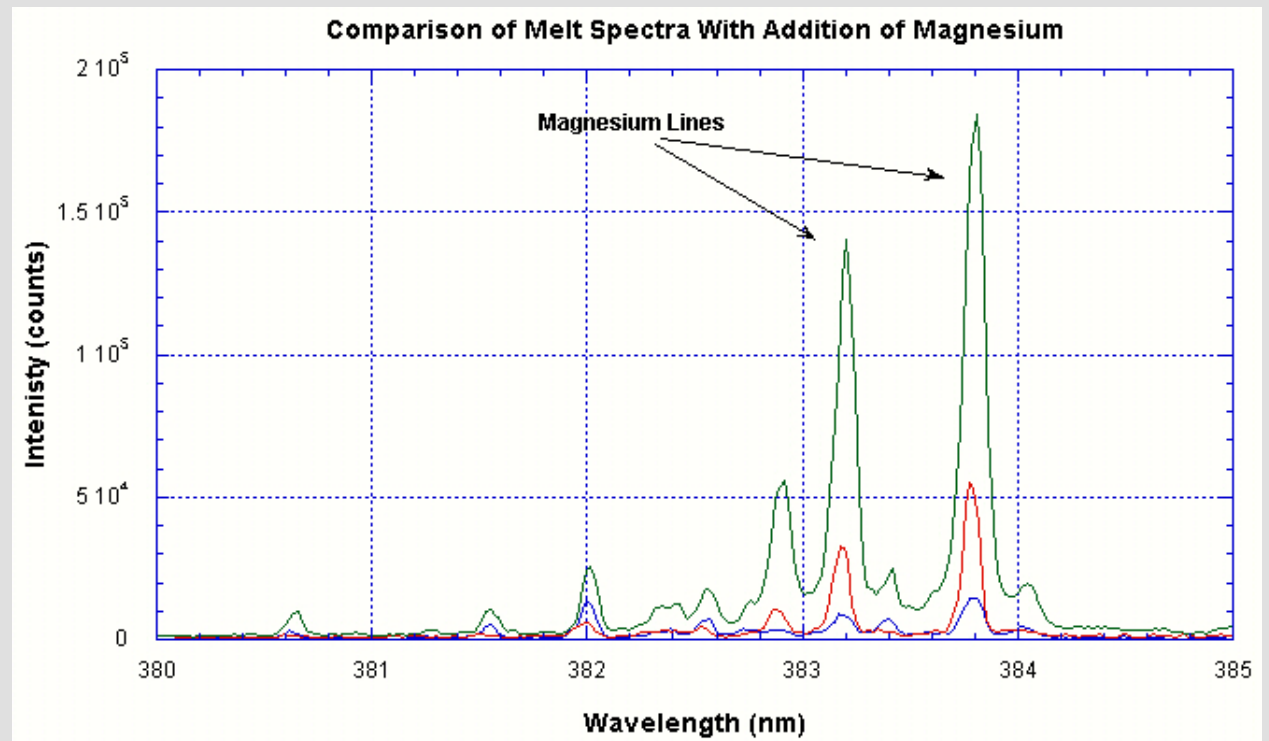
Pilot Scale Test: Concentrations



Element Ratio	Baseline Ratio	Calibrated Ratio
Fe/Al	0.0078	0.0079
Mn/Fe	0.51	0.504
Cr/Al	0.0003	0.0003

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Pilot Scale Test: Alloying



Element Ratio	Added Percentage	Calibrated Ratio Increase
Mn/Fe	0.2%	0.21% ¹
Mg/Fe	0.2%	0.32% ¹

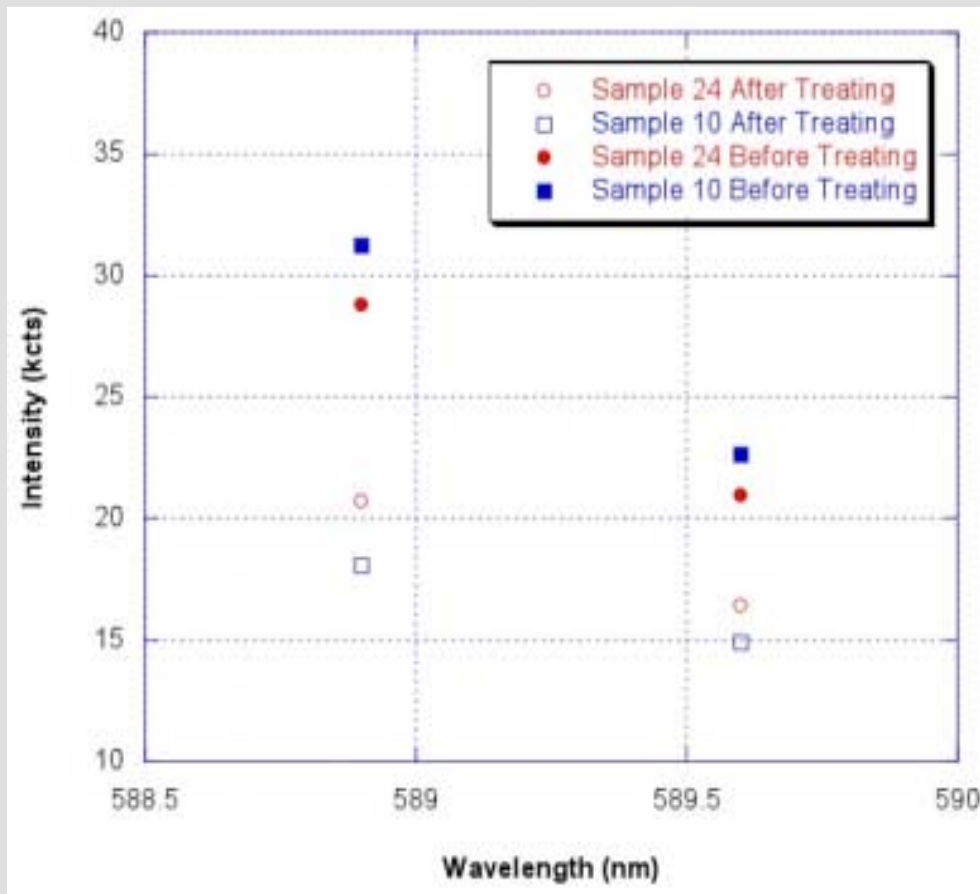
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Industrial Application

- A primary aluminum specification calls for sodium concentrations below 40ppm
- Therefore all aluminum is treated with sodium-reduction process
- LIBS probe can eliminate unnecessary processing with instant sodium measurement
 - **Reduced costs**
 - **Increased Productivity**

Industrial Application

- **Initial Sodium Measurement**
 - LIBS is capable of measuring sodium concentrations at single ppm levels

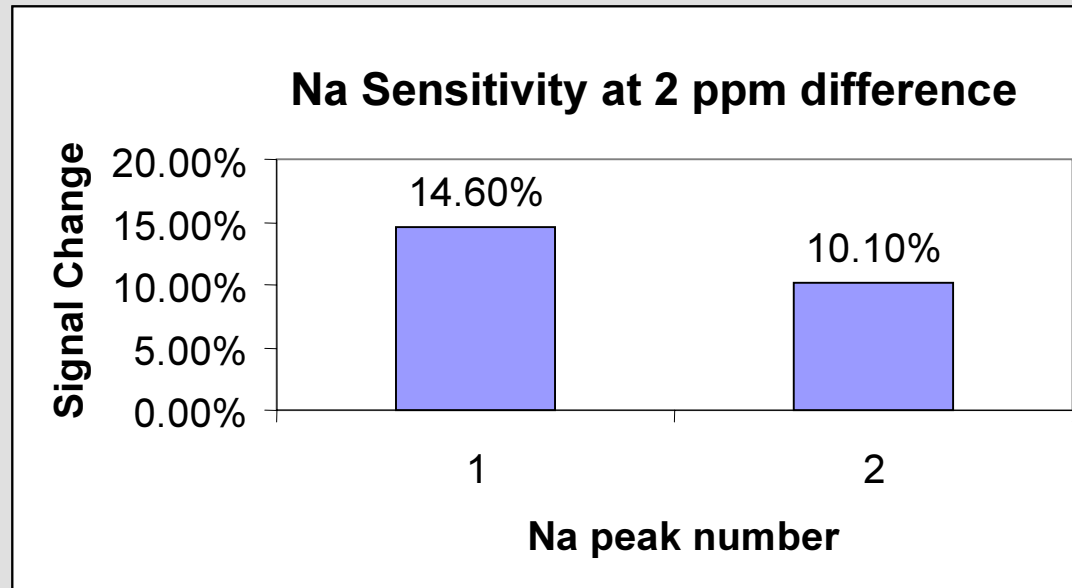


- **Sample 10: 8ppm**
- **Sample 24: 10ppm**

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Industrial Application

- **Initial Sodium Measurement**
 - LIBS is capable of discerning between very low sodium levels

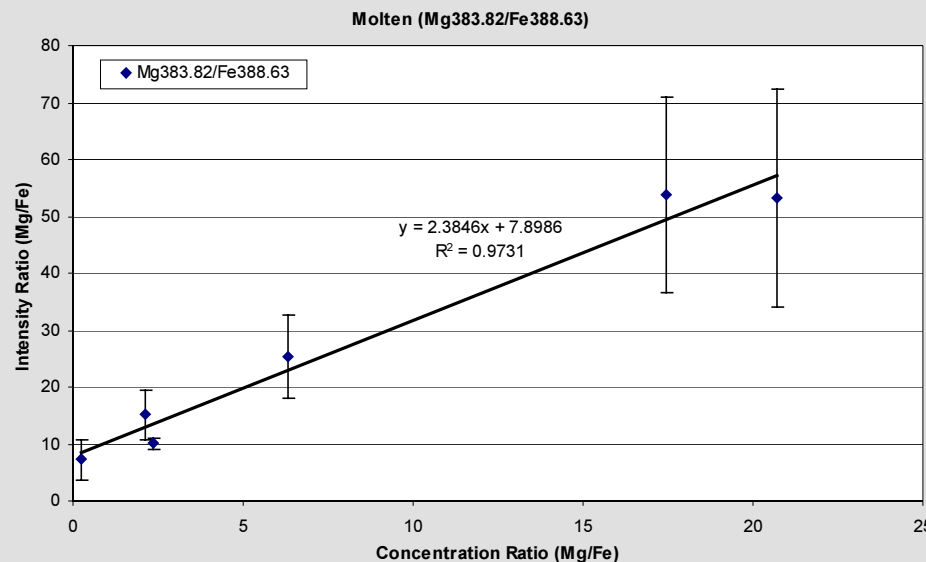


- **Sample 10: 8ppm**
- **Sample 24: 10ppm**

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Software Developments

- LIBS spectra are typically translated to concentrations with calibration curves
- Calibration curves are not robust
- Calibration curves are most accurate when measuring ratios
 - **Need to know concentration of one component *a-priori***
- Calibration curves are less accurate as concentration increases



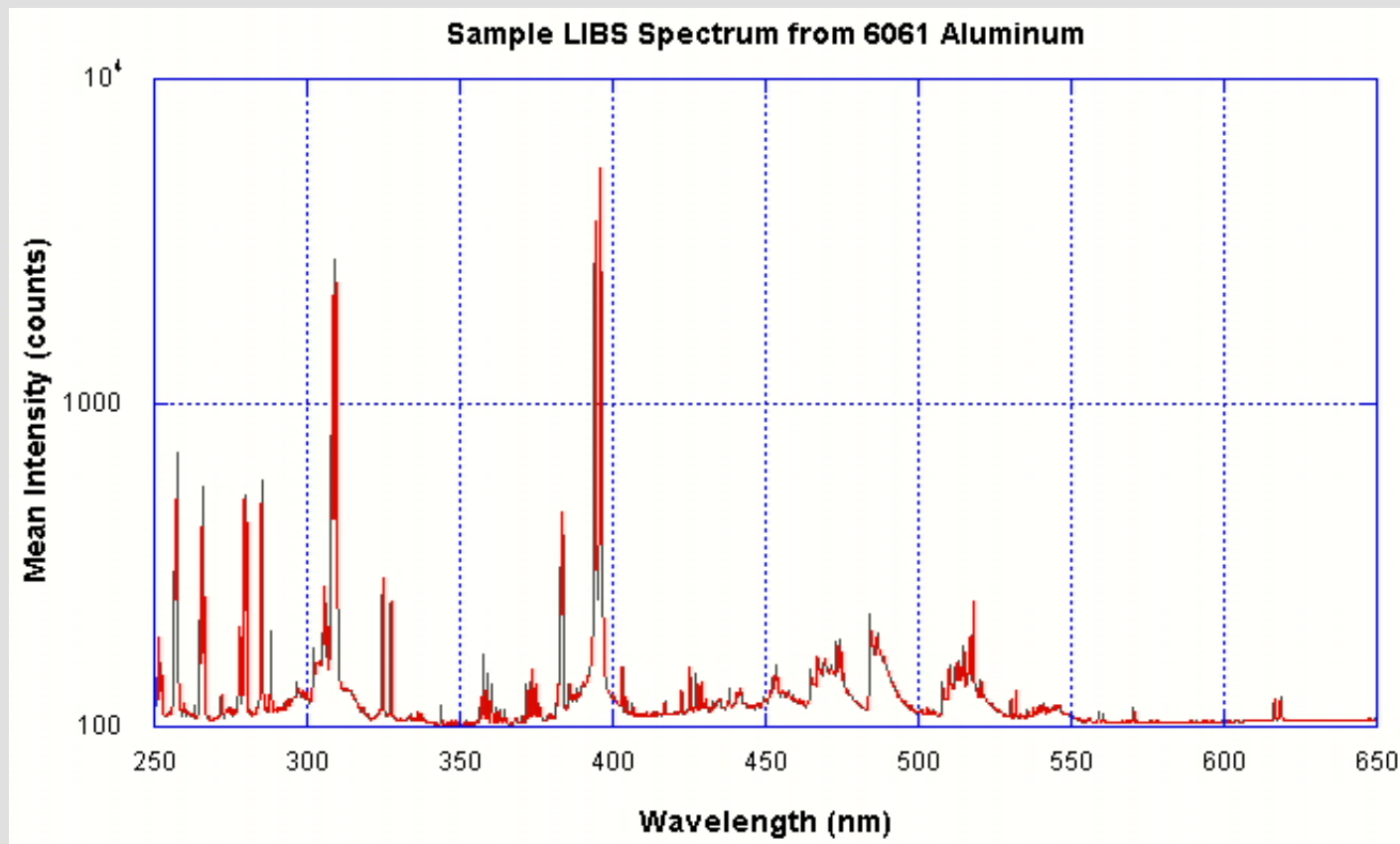
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Software Developments

- ERCo is pursuing a proprietary algorithm that translates LIBS spectra into concentration measurements
- Method applies to both molten and solid states
- Method is independent of experimental parameters such as laser power
- No calibration data required
- Actual concentrations are computed rather than ratios
- Sample material does not need to be specified

Software: Initial Results

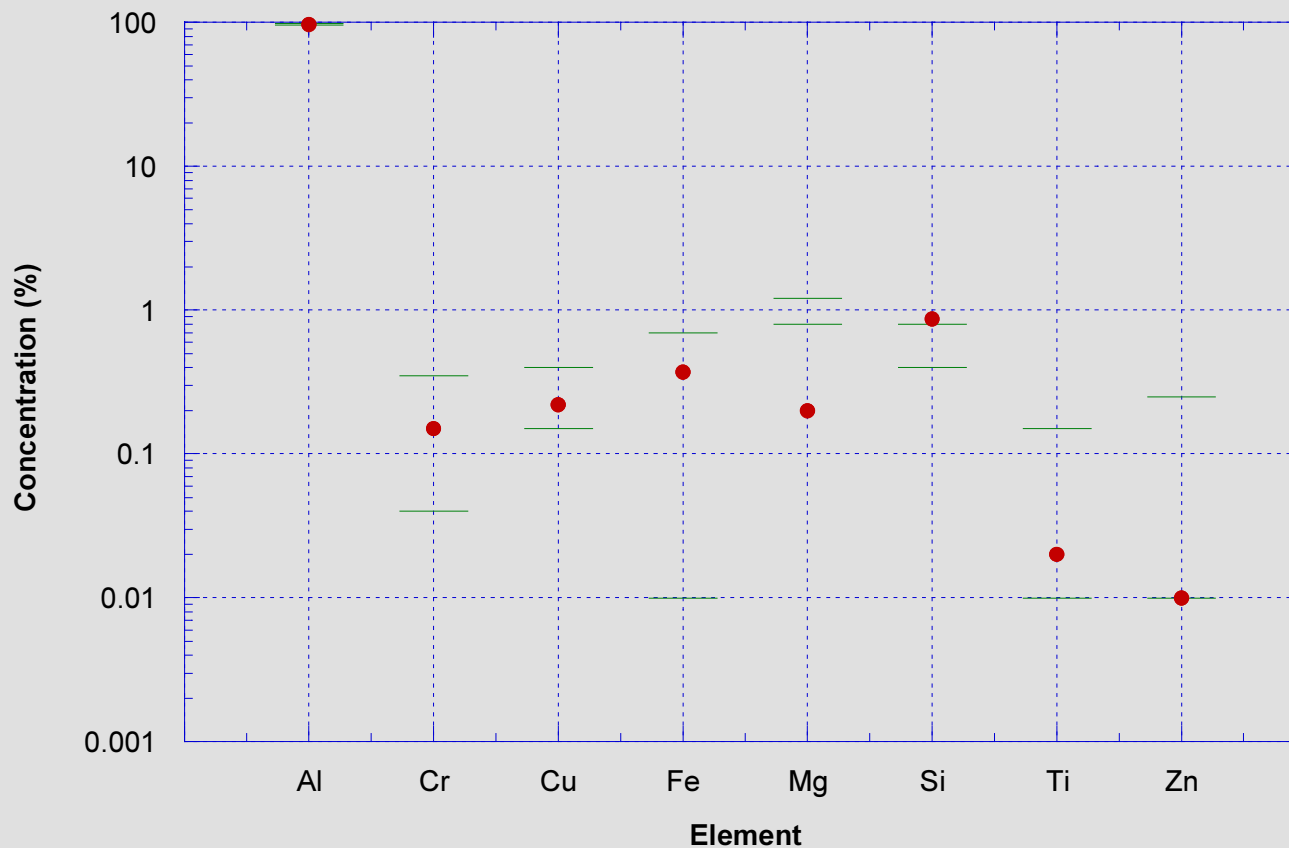
- Initial software results from 6061 aluminum alloy plate



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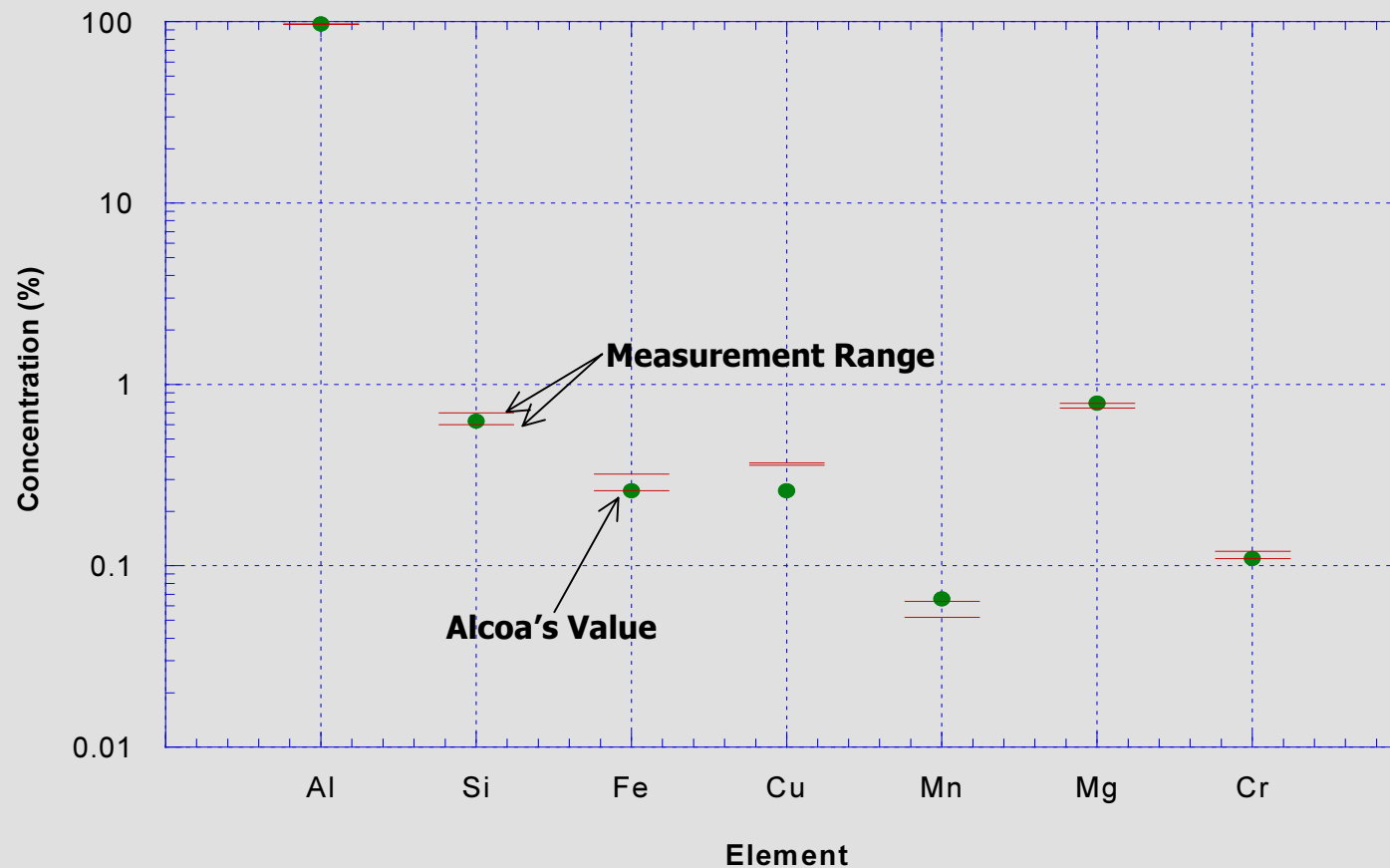
Software: Initial Results

- Initial software results from 6061 aluminum alloy plate



Software: Recent Results

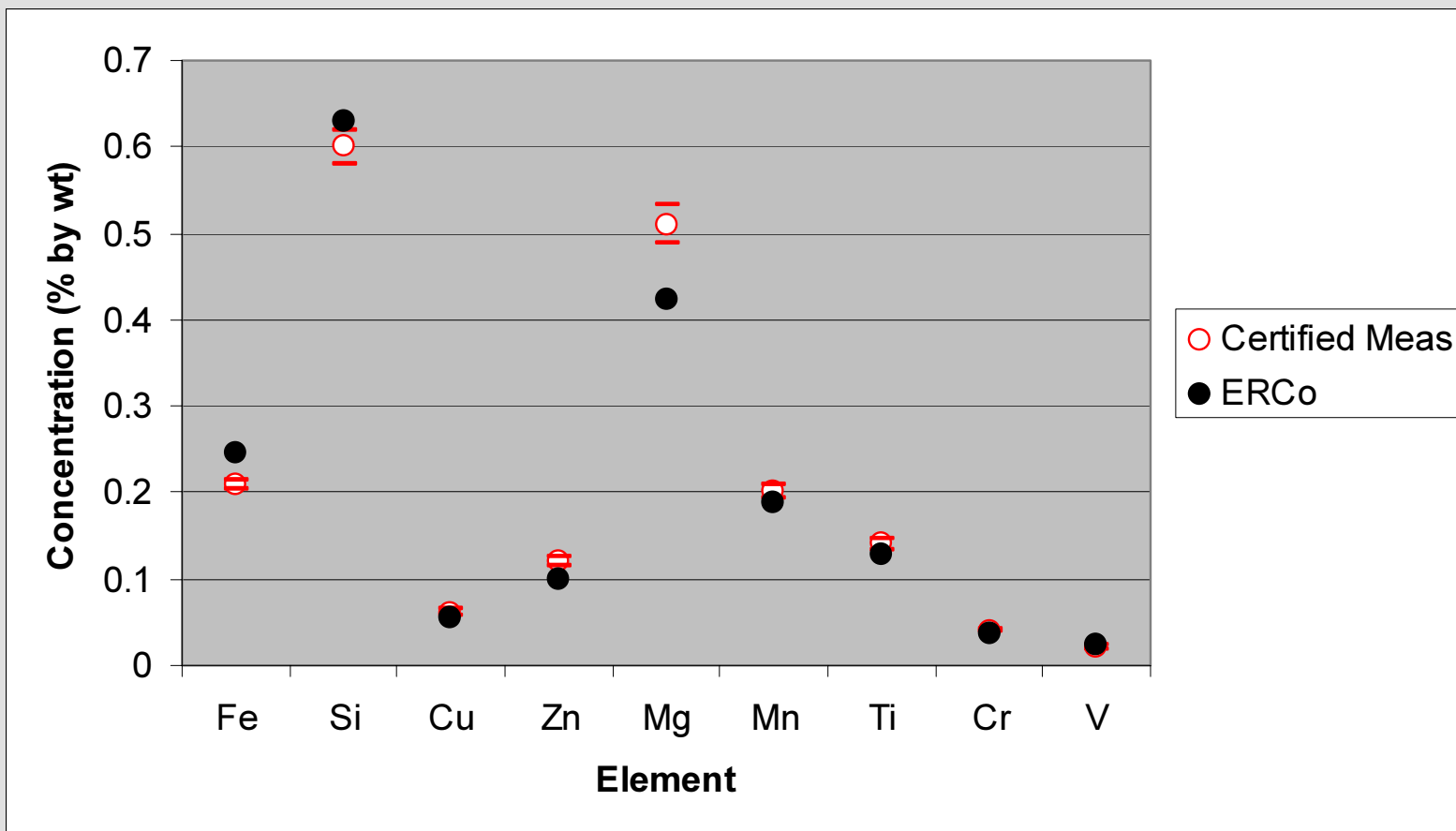
- Recent aluminum alloy test results in comparison to commercial analyzer



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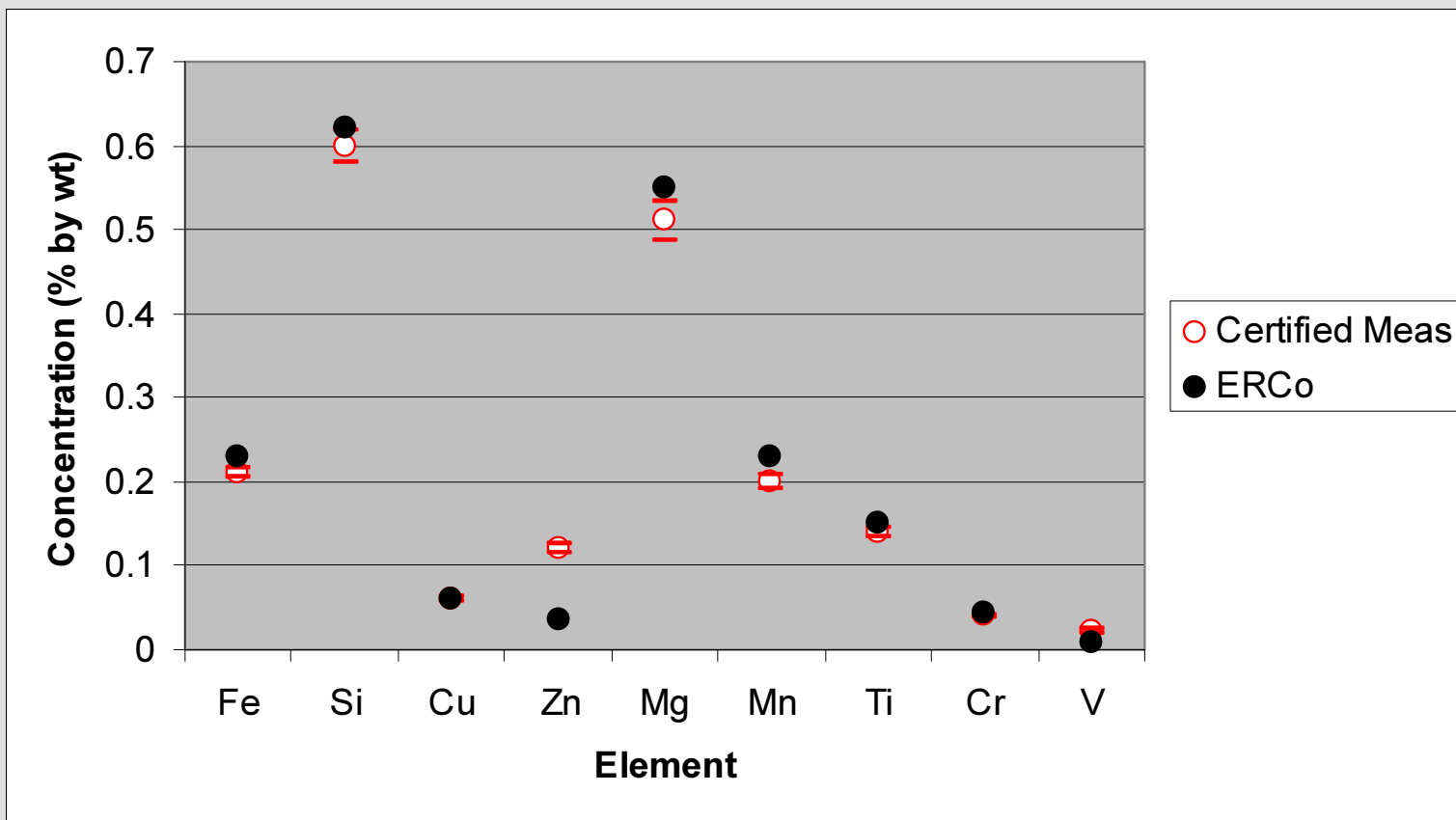
Software: Recent Results

- Comparison to certified aluminum standard

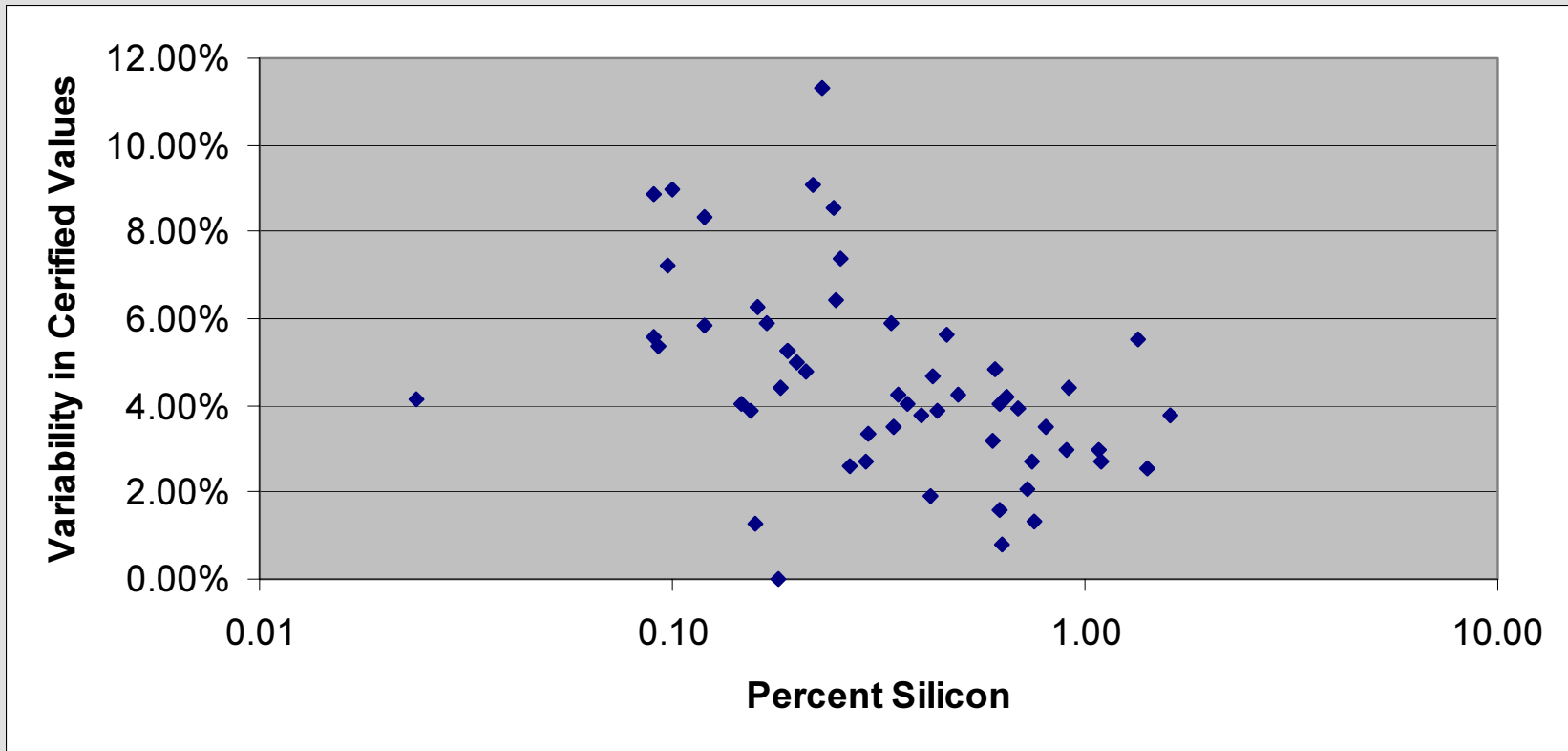


Software: Recent Results

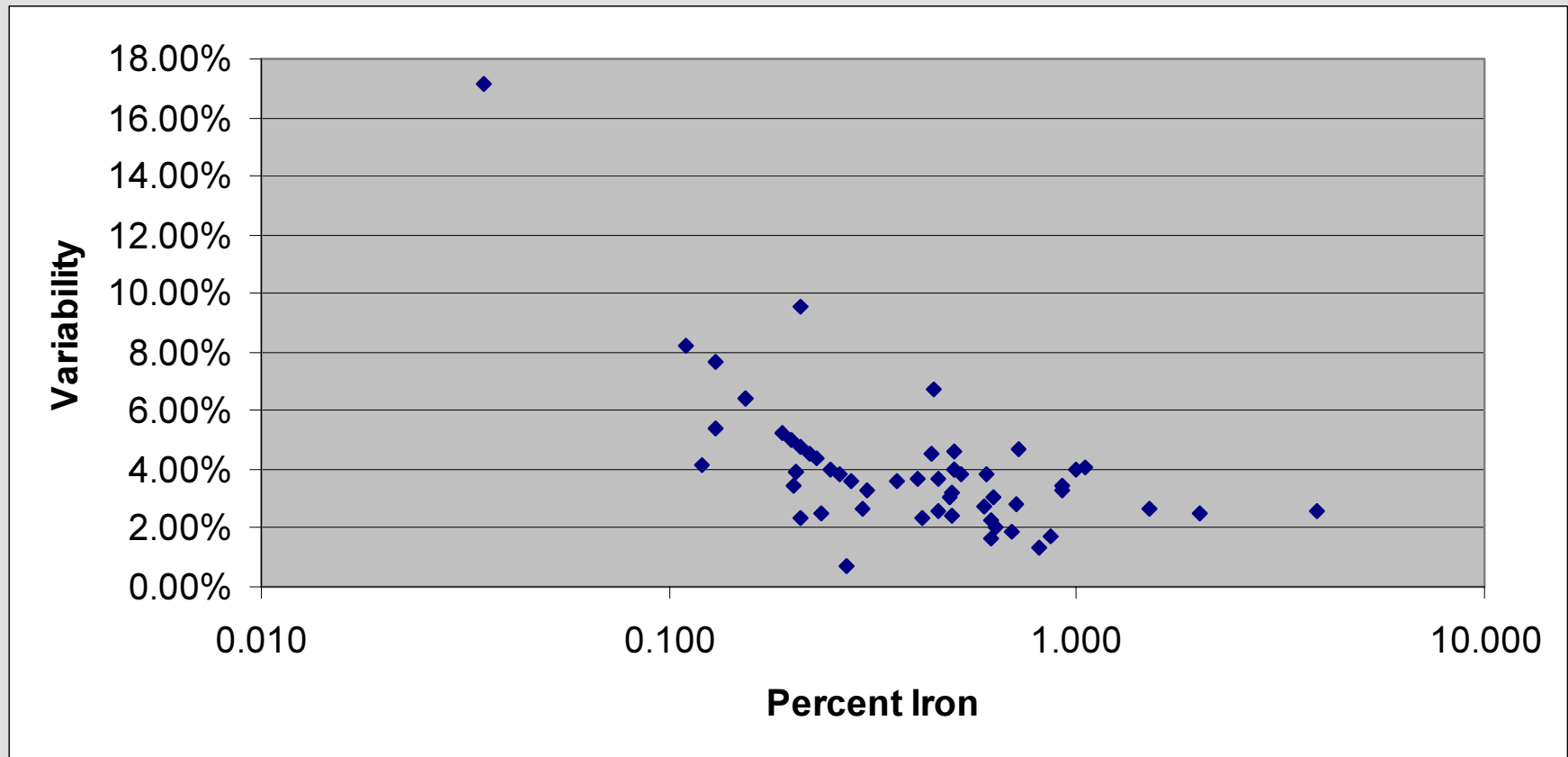
- Comparison to certified aluminum standard



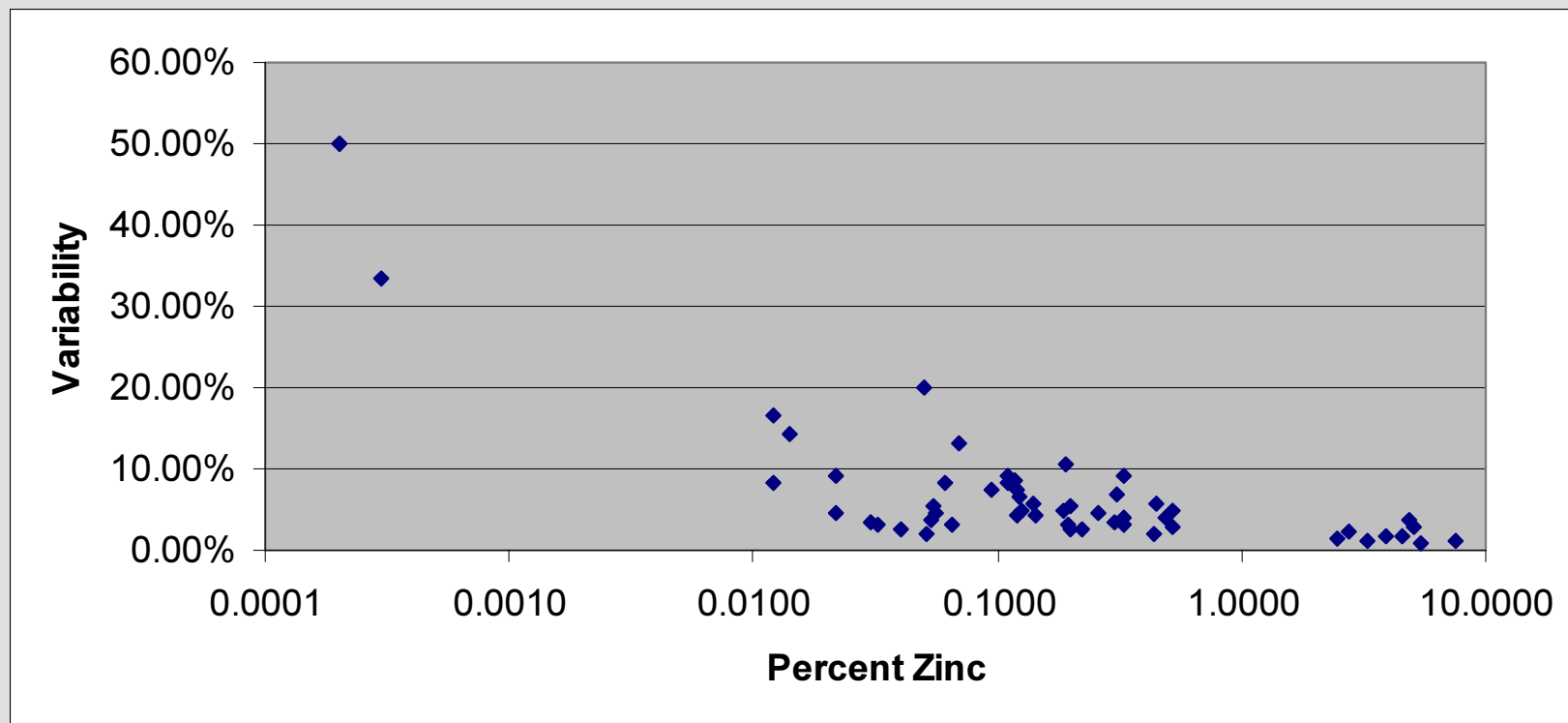
Variability In Certified Standards



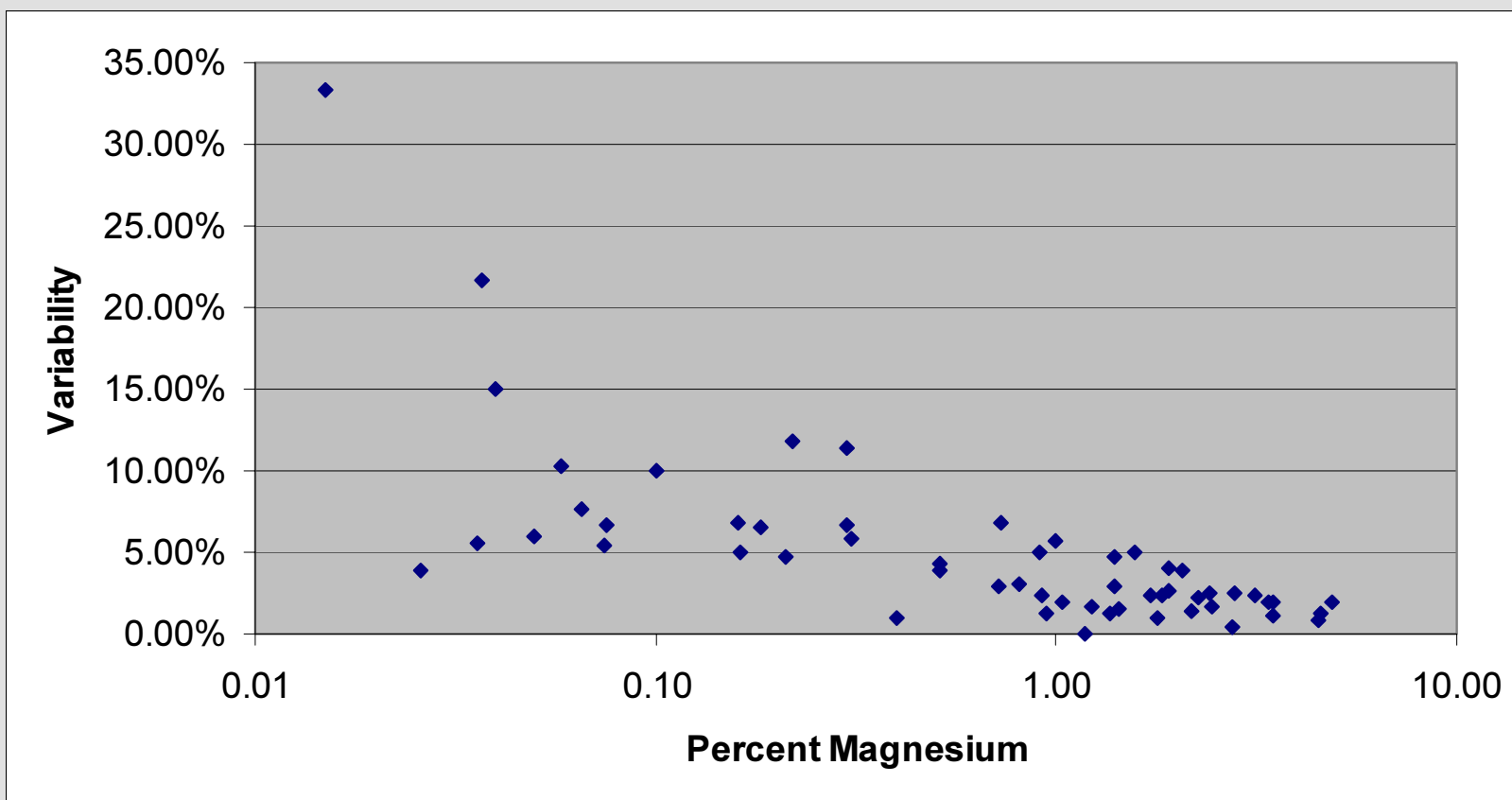
Variability In Certified Standards



Variability In Certified Standards



Variability In Certified Standards



Variability In Certified Standards - Conclusions

- When present under 1%, certified standard variability is as high as 25%
- Confidence at any concentration cannot be less than 2-3%
- When comparing LIBS probe to certified samples these uncertainties must be taken into consideration

Improvements and Upgrades

- Industrial grade components
- Novel optical design
- Improved precision and repeatability

Industrial Grade Components

- **Fiber optic coupled laser**
 - **Industrial Design**
 - **Low Maintenance**



Improved Hardware Design

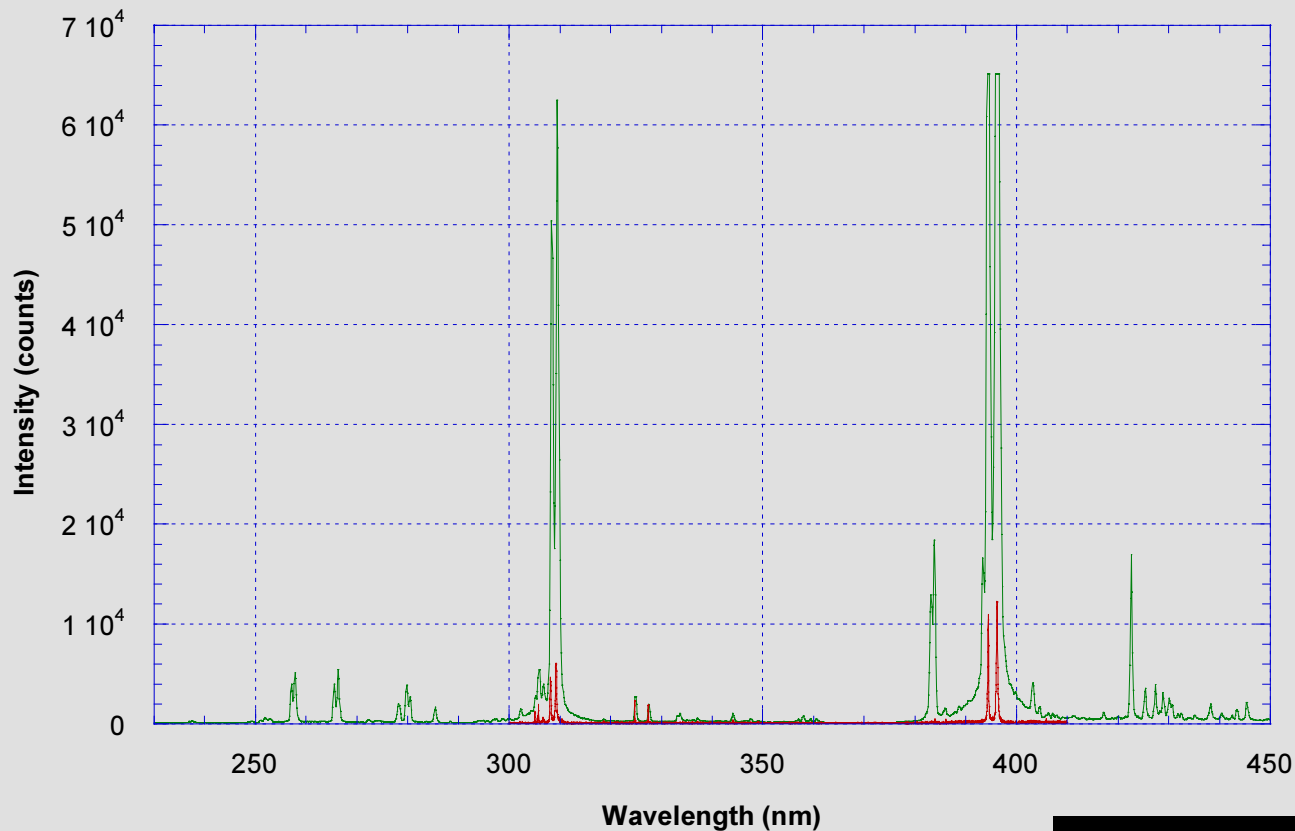
- **Improved Cooling System**

- **Cooling circuit overhauled so that inexpensive compressed air can be used to cool the probe**
- **Operating temperatures inside the probe reduced from 650°F to 300°F with 50psi of pressure**
- **Less heat-related degradation of components expected as a result of these improvements**

Improved Optical Design

- **Enhanced Accuracy**

- **Optical component upgrades dramatically increased signal strength**

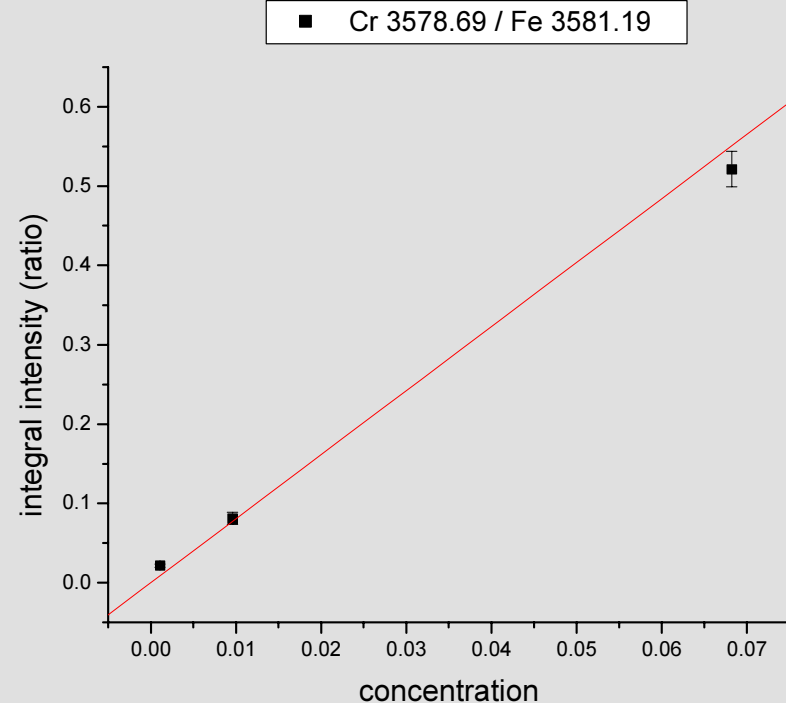
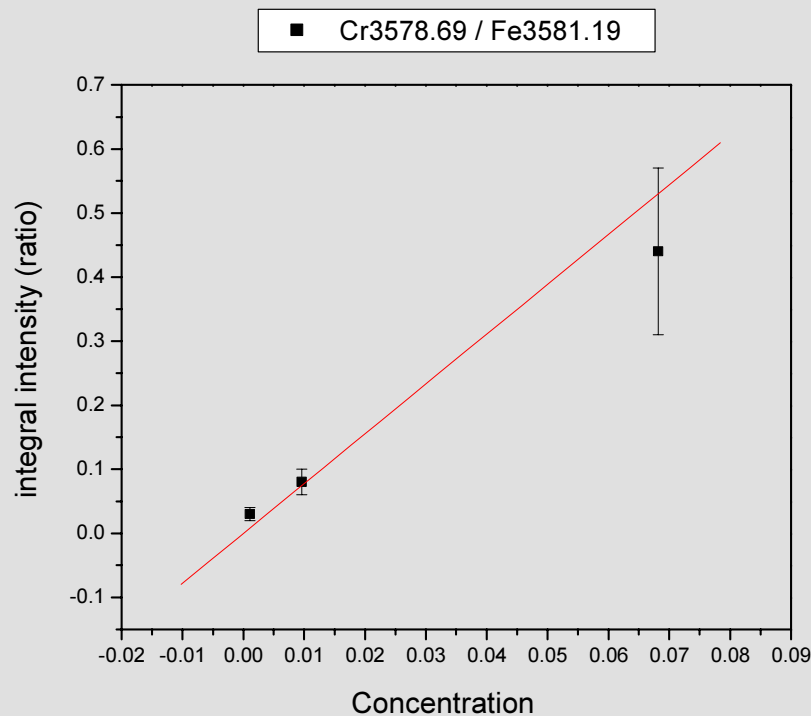


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Improved Optical Design

- **Enhanced Accuracy**

- Increased repeatability and accuracy

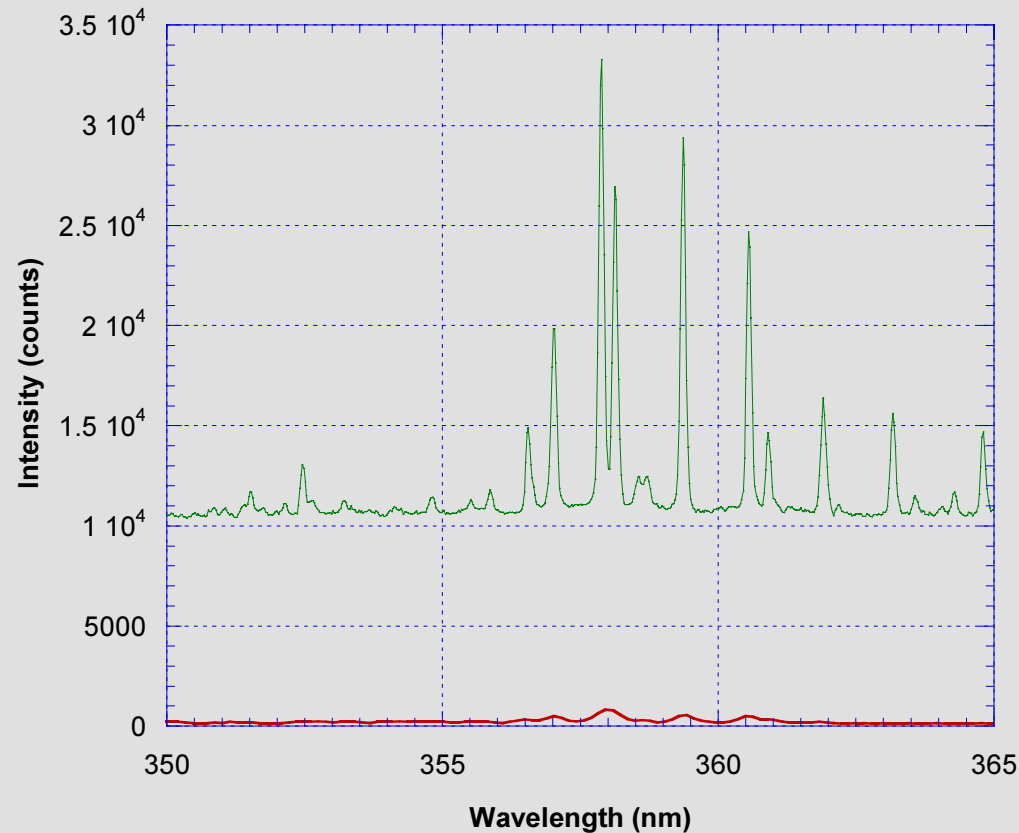


Loss of repeatability at higher concentrations is common in LIBS data

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Improved Optical Design

- **Signal Jump Using Improved Optical Design**



Large Increase in Signal Where Poor Response was Previously Seen

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Commercialization

- **Proposed plant tests/deployments, and planned use in IOF manufacturing plant(s)**
 - Demonstrations planned at:
 - Commonwealth Aluminum
 - ARCO Aluminum
 - Century Aluminum
 - PPG (Fiberglass)
- **Commercialization path & partners**
 - ERCo will manufacture and license marketing and sales
 - Stein Atkinson Stordy will commercialize overseas
 - Patent filed

Performance Merits

- **Improving energy efficiency**

- How will energy be saved?

- Furnace idling during chemistry analysis eliminated
 - Product rejections due to off-spec chemistry reduced

Aluminum Energy Savings

- **Production increase of 72% due to continuous furnace operation and commensurate reduction in specific fuel use**
- **Eliminated idle time – 34% savings**
- **17 Trillion BTU savings annually by 2010**

Glass Energy Savings

- In 1995, percent packs were 85-93%
- 25 to 53 Trillion BTU expended
- LIBS could increase percent packs to 98%
- 17 to 45 Trillion BTU savings annually

Steel Energy Savings

- **Nearly 3% of all product is scrapped or downgraded**
- **1/2 of the downgraded scrap is reworked – 26 trillion BTU per year wasted**

Path Forward

Future Technical Milestones

Milestone	Due Date	Completion Date	Comments
Construction of demonstration probes	9/02		On schedule
Refine and automate software	9/02		On schedule
Complete in-house testing	10/02		Not yet scheduled to begin
Installation in aluminum plant	11/02		Not yet scheduled to begin
Complete in-plant testing	2/03		Not yet scheduled to begin

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Path Forward

- **Next steps**

- Complete construction of probes for installation at aluminum plant
- Complete refinement of algorithm and construct user interface
- Complete in-house testing

- **Go/no-go consideration(s)**

- Algorithm accuracy
- Sensor durability

Conclusions

- **Collected Concentration Data from Molten Aluminum**
- **Calibrationless Software Results are Promising**
- **Three Industrial Host Sites Signed Up**
- **Probe Design Improved and Operational**
- **Optical Design Improved and Operational**
- **Signal-to-Noise Ratio Dramatically Improved During Program**